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IGNITION POINTS AND COMBUSTION REACTIONS IN DIESEL ENGINES

By J. Tausz and F. Schulte

PART I

Communication from the Petroleum Research Laboratory
of the Institute of Applied Chemistry
Technical High School, Karlsruhe

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PART I.

Introduction

The utilization of liquid fuels in internal combustion engines assumes ever greater proportions, since the transformation of heat of combustion into mechanical energy has been the most successful in this field. In ordinary combustion, intermediate reactions and products are not significant for practical purposes and the heating value is the information of interest, whereas with combustion in the engine, the possibility of using a fuel and its utilization depend entirely upon the course of combustion, so that the chemical reactions before and during the combustion become decidedly significant. From this standpoint, only those fuels with certain definite properties are useful in internal combustion engines.

With the exclusion of gas engines, internal combustion engines were originally constructed for use with gasoline as a working medium since it was cheap and available in large quantities. The gasoline which is so valuable today, was originally a by-product in petroleum refining and in the distillation of

*Communication from the Petroleum Research Laboratory of the Institute of Applied Chemistry, Technical High School, Karlsruhe. For Part II, see Technical Memorandum No. 484, which follows.

the crude oil as much gasoline as possible was disposed of in the kerosene, which was the main product. Thus kerosene, rich in gasoline, was put on the market and various countries were forced from the standpoint of safety to legislate on its flash point. This method of disposal of the gasoline, while still partially existent to-day, has been superseded on account of the enormous growth of the motor industry, which has rapidly made gasoline the most valuable petroleum product. The boiling range of gasoline has been considerably displaced for the same reason, and to-day it frequently contains in appreciable quantities portions belonging in the kerosene fraction, which are not so suitable for combustion in the engine. The production of straight-run gasoline lags far behind the constantly increasing demand, so that other fuels are used to make up for this deficiency, as well as the production of gasoline from higher boiling petroleum fractions by cracking, and by the $AlCl_3$ process, among others.

This gives rise to the important question as to whether the fuel should be adapted to the engine by producing petroleum products suitable for the engine through chemical processes on the present fuels or whether it is possible to improve equipment such as carburetors and engines so that as much of the crude as possible may be used without further transformation. This second possibility has the advantage of greater energy economy since the transformation of the high boiling petroleum products into gasoline results in loss of material and necessitates util-

ization of heat. Further, for engines using heavy oil, in which class the Diesel engine has shown greater superiority, suitable petroleum and lignite tar oil products are scarce and difficulties arise when coal tar oil and similar products are used, due mainly to the course of the combustion reactions. Thus technical progress demands with increasing urgency scientific research and explanation of the combustion reactions and the factors which influence them.

A. General Part

1. Significance of the Ignition Point

Various factors play an important part in the complete combustion of fuel in an engine. The ignition point is of decisive significance in connection with the utility of fuel oils. All organic substances can autoignite when mixed with air or other oxygen-containing gas without the aid of an igniting mechanism or mechanical work. The lowest temperature at which autoignition occurs is called the ignition point of the substance. The ignition point should not be confused with the flash point or the burning point. The flash point is the temperature at which flashing of the fuel is observed when brought in contact with an igniting flame. The burning point is the temperature at which the fuel burns further after flashing. Although these two physical constants are particularly important in the case of liquid fuels, they bear no relation to the ignition point. As evidence of this, the inflammability can increase with decreasing ignition

point. The inflammability depends upon the vaporization of the fuel, of which the ignition point is independent.

The simplest case of ignition is that of gases as it occurs in practice in the gas engine. It is the most available exact investigation, since homogeneous mixtures are concerned, and it has been the subject of numerous exhaustive and successful researches. Nevertheless, we are far removed from an entirely clear understanding of it, for the velocity of reaction is enormously fast. However, the possibility of intermediate stages is very limited, in opposition to the ignition of liquid fuels, where all possible intermediate reactions must be assumed. Concerning the chemical processes involved in the ignition of substances of larger molecular weight, such as liquid fuels, practically nothing is known and a large field lies open for chemical investigation. The problem is a difficult one for, on ignition of such substances, during the shortest period of time the most different and most complicated chemical transformations and reactions occur, since these liquid fuels are mixtures of various chemical individuals which are only very incompletely known.

As already mentioned, the ignition point of the fuel used is conclusive for establishing the commencement of the explosion in the engine. The matter in question is the interpretation of its limitations with the most diverse substances and mixtures on the one hand and pressure and temperature relations on the other.

In the explosion engine the fuel-air mixture formed in the carburetor is sucked in, compressed and ignited, usually with an electric spark. The gas pressure produced by the combustion drives the piston. The velocity of the piston can be so high that at the beginning of the downward stroke, the combustion is not yet completed. The velocity of propagation of the ignition - the explosion velocity - is concerned here and would limit the number of revolutions if other mechanical factors did not enter into consideration. The cause of the so-called knock is partially to be sought in the fact that, due partly to contact of the compressed mixture with the hot cylinder and partly to heat of compression, a temperature is reached at which ignition occurs prematurely of its own accord. The mixture thus ignites before the piston reaches the proper position and this not only results in a very wasteful expenditure of energy in consequence, but also is harmful to the engine. The higher the ignition point of the fuel used, the less readily does autoignition occur in the engine. Frequently cracked gasoline is inclined to give autoignition, particularly if it contains portions of the kerosene fraction. It is possible to overcome the objectionable occurrence of detonation if the temperature at which autoignition occurs - the ignition point of the fuel - is raised by blending. Recently efforts have been made to add substances which even in very small amounts have a large influence and which affect the first phase of the combustion. Research on these anti-knock

materials is being conducted at Karlsruhe at the present time, and we hope to be able to report more about this later.

With Diesel engines, the fuel is sprayed into the compressed air and autoignition occurs in the heated mixture. In this case also, the ignition point is decisive since it determines the final compression pressure which it is necessary to produce. Since fuel is constantly sprayed during the ignition, whereby the Diesel engine works as a constant pressure engine, the velocity of propagation of the ignition also plays a part here.

The engines, designated as explosion and Diesel, thus require opposite properties for their operating substances. The gasoline engine requires a fuel with as high an ignition point as possible in order to be able to work at higher compression. The Diesel engine demands a fuel with as low an ignition point as possible. With the gasoline engine the vaporization of the fuel and inflammability, that is, easy burning of the fuel-air mixture by the ignition flame, are naturally further very important factors, whereas with Diesel engines, these play no part.

In recent years, ignition point measurements have been adopted more and more as a criterion for the utility of various oils in engines. In this connection, the fact has not yet been generally recognized, that the ignition point is influenced in a frequently unexpected way by the most varied chemical and physical conditions. The ignition point depends on the pressure at the point of the compression. Research on these anti-knock

The transformation and decomposition temperature of the fuel, the varied reactivity of the resulting intermediate products thereby determined, the reaction velocity itself influenced by all of these factors, the chemical structure, extent of saturation, size of the molecules and many others, affect the ignition point decidedly.

In order to obtain to some extent an insight into this problem, the procedure and apparatus used in the ignition point measurement must be accurately developed and established, which has not been done in previous measurements. Further, it was necessary to determine the ignition points of accurately defined substances, not useful technically, in order to obtain constants and to evaluate the activity of such compounds as are either present in small quantities in fuels or are frequently formed during or shortly before the ignition and which influence it.

We measured the ignition points of numerous substances, not previously investigated, in particular of chemically homogeneous substances, both with and without pressure and sought to provide fundamental information through study and compilation, according to series, of the ignition points of various groups of organic chemicals, such as the hydrocarbons, aldehydes and ketones, alcohols, acids and acid anhydrides, and so on, so that fuels blended from these various compounds and arbitrarily mixed could be evaluated from the standpoint of their utility in the engine and so that the way may be paved for the utilization in the engine of

products not hitherto useful by blending according to predetermined means.

Moreover, the main object in view was the influence of increase in pressure on the ignition point. Hitherto ignition point measurements have almost all been made at ordinary pressures. In the course of an investigation it appeared that small fluctuations in the barometric pressure often had an appreciable effect on the manner and the temperature of ignition. From that it can be judged how different the ignition points must be at atmospheric pressure as they are almost always measured and in the Diesel engine. Ignition point measurements at atmospheric pressure cannot be conclusive for the evaluation of a fuel for use in an engine since the ignition points are frequently affected in an unexpected manner on increasing the pressure. For example, addition of other substances, which lower the ignition point at ordinary pressure, may raise it at an increased pressure such as prevails in the Diesel engine. This has also been shown in practice. Thus, for example, mixtures of priming oil with tar oil in practice do not give favorable results*, whereas the ignition point examination at ordinary pressure indicates an extensive lowering of the ignition point. Very frequently it results that such a lowering of the ignition point does not continue on application of pressure, such as prevails in the engine. Therefore ignition point measurements under pressure were accord-

*P. Rieppel, "Research on the Use of Tar Oils for the Operation of Diesel Engines." Mitt. Forsch. Verein. deut. Ing., Vol. 55.

ingly undertaken by us under conditions as similar as possible to those actually prevailing in the Diesel engine and for this purpose a simple apparatus along the same principles was devised.

From several investigators it would be assumed that the pressure under which ignition occurs in the engine, is without appreciable effect on the ignition point or that it changes in a constant manner with increasing pressure. Thus Alt* has given a formula, according to which the ignition point in the engine can be computed by multiplying by a factor the temperature obtained in the measurement in the crucible. Such a formula and the value thus obtained are not useful. The influence of pressure is very appreciable and the ratio of the absolute temperature in the engine under pressure to that in the ignition point apparatus at ordinary pressure is not constant for different fuel oils as Alt and others assume. The change in the ignition points of various substances with increasing pressure is very different. In fact, fuels designated by the same name, as, for example, various gasolines and various kerosenes, differ very appreciably with respect to the change of their ignition points with increasing pressure on account of the differences in their composition. For the most part, the ignition point is lowered on increasing the pressure. However, there are many substances with which it is raised to a certain degree. Therefore, as already mentioned, ignition point measurements under pressure only are capable of evaluating motor oils. Clearly with mixtures

*Zeitschrift des Vereines deutscher Ingenieure, 67, 686 (1923).

which are frequently employed to transform a material with too high an ignition point into one more useful, this is very evident. Whereas at atmospheric pressure the ignition points are lowered to a large extent by the addition of very small quantities of an easily ignitable substance, frequently these additions cause no lowering at high pressure and in fact, the ignition point can even be raised. Our researches show, for example, that a mixture of 20% of an easily ignitable shale oil or lignite tar oil with 80% of a coal tar oil, not readily ignitable, can have a higher ignition point under pressure than the pure coal tar oil. Small additions of lignite tar oil or shale oil to coal tar oil, which lowers the ignition point at ordinary pressure to a marked extent has, in general, almost no value for Diesel engines under pressure.

From our work it appears that the most economical way to use fuels is always with mixtures. However, mixtures containing less than 50% of an easily ignitable oil are rarely of value. Smaller additions have usually no favorable effect on the ignition point.

2. The Chemical Reactions During Ignition

The chemical reactions which take place before ignition commences are extremely numerous. With many substances the ignition point is so low that preliminary decomposition cannot occur but the vapor or fog of the original substance ignites.

With some substances thermal decomposition occurs before ignition. The decomposition products thus produced can have different effects. If, for example, one of these decomposition products has a particularly low ignition point, then it depends upon the quantity of this substance formed and the heat developed on its ignition as to whether it acts as an initial igniter in bringing the residual substances to ignition or whether it would require a higher temperature. In opposition to the substances which form decomposition products before ignition, there are some which polymerize and thereby have a high ignition point.

Some substances split off hydrogen, in particular those with high ignition points as exemplified by the aromatic hydrocarbons. If the products thereby formed have a higher ignition point than hydrogen, the hydrogen will act as an initial igniter and the ignition point of the substance will approach that of the hydrogen split off.

Combustion is the process of taking up oxygen with loss of heat. It can occur very slowly as in the case of animal organisms or its velocity can be so rapid as to cause explosion. The ignition point is not the point where oxygen combines with the substance concerned, but is the point where the velocity of this reaction becomes so great that complete combustion occurs almost instantaneously.

We can assume that a silent invisible combustion occurs be-

fore each visible ignition. This reaction is practically imperceptible at ordinary temperature since its velocity is low and the heat energy produced is dissipated. The reaction velocity increases, however, with pressure and temperature and since the reaction itself increases the pressure and temperature, the velocity increases until ignition occurs.

With substances of high molecular weight, which have a low ignition point, we must assume that oxygen-containing organic compounds such as aldehydes, acids, and acid anhydrides are first produced which, in consequence of their very low ignition points initiate sudden combustion, although they are only produced during this short time in limited quantities. Such oxygen compounds form more rapidly and in larger amounts in the case of unsaturated compounds. These can be present from the beginning or they can originate by decomposition of saturated compounds. From these oxygen products others can form, which within a very short momentary range of pressure and temperature are steadily and so rapidly decomposed again that it has not as yet been possible to prepare them and therefore they have not been taken into consideration in explaining the processes of ignition. This is the case with addition of oxygen to form molecular oxides and peroxides.

It is known that organic substances, in general, even saturated compounds, should not be permitted to be in contact with oxygen under high pressure, since there is always the possibility

that through formation of molecular oxides and their transformation products, the peroxides, an explosion of the strongly endothermic system may occur in consequence of initial ignition. Such molecular oxides form very slowly at ordinary temperature, while at higher temperatures, their production has not as yet been successful due to their instability. Nevertheless, one can very well consider that, with ignition on heating a fuel, the zone of peroxide formation is rapidly advanced and it reaches the stage of initial ignition on account of the formation and instantaneous decomposition of even these very small amounts.

The formation of molecular oxides (peroxides) occurs to an appreciable extent with many chemical substances, which also exist in cracked oils and influence the ignition point in a decided manner. Further unsaturated compounds, which form molecular oxides or peroxides, are produced by thermal decomposition of saturated substances such as paraffin, so that one must assume that the ease of peroxide formation from the decomposition products determines the low ignition point of the easily decomposed substances, and not the decomposition itself as Holm assumed. Substances which readily take up oxygen with formation of molecular oxides have therefore the lowest ignition points. Then on the decomposition of these, which occurs very easily and explosively, so much heat is generated that it suffices to bring the whole mass to the point of ignition. In the manufacture of explosives the detonation temperature is understood to

be that at which an initial igniter will explode without mechanical assistance. In a large series of organic compounds, the height of the ignition point frequently depends upon the detonation temperature of the oxygen products formed. The initiation of explosion must also depend on the quantity of the initial igniter formed. The greater therefore the partial pressure of the oxygen, the more molecular compounds can be formed, so that in general the ignition point in pure oxygen is lower than in air.

On the other hand, at higher partial pressures of oxygen, it can happen that, before the oxygen-containing substances already formed decompose or ignite, they react further with oxygen forming a material of higher detonation temperature, whereas with lower oxygen partial pressure, such as in air, decomposition occurs, before these silent additional oxygen reactions take place. The paradoxical case then appears that the ignition point in pure oxygen is higher than in air.

The ignition point accordingly would be lowered by very small quantities of peroxide-forming substances. In general compounds with olefinic double bonds are particularly suited for peroxide formation just as are the oxygen-containing substances, which are inclined to form oxonium compounds. Unsaturated compounds can be formed by decomposition of saturated ones. The possibility of decomposition increases in the case of aliphatic substances with increasing number of carbon atoms and the decomposition occurs at correspondingly lower temperatures as

the size of the molecule becomes greater. This is also the reason why the apparently stable paraffins ignite with considerably greater ease than the lowest boiling gasoline and why the ignition point generally drops with increase in the size of the molecule.

It can be established that peroxides are actually formed but whether these are organic molecular oxides, true peroxides, or hydrogen peroxide, cannot be decided. However, this does not alter the conception of the process since hydrogen peroxide as well as organic peroxides also should influence the ignition in the presence of organic substances.

Experiments were so conducted that the air flowing into the ignition block (See Part II, Technical Memorandum No. 484 - Experimental part) passed through a very short glass tube attached to a wash bottle. This contained 5% potassium iodide solution slightly acidified. At various temperatures just below the ignition point, a rapid stream of air was sucked through both the ignition block and the wash bottle by means of an aspirator. The fuel was added in drops as in the ignition point measurements, or in the case of solid substances in very small quantities by means of a spatula. Mixing of the vapors with air occurred in the crucible. The formation of peroxides could be established by the liberation of iodine in the potassium iodide flask, the iodine being identified in this work by means of starch.

Paraffins took up oxygen even at 150°C and the displaced hydrogen burned to water. Peroxide formation commenced at 250°C and was greatest at 300° , the liberation of iodine being considerable. If iodine is liberated and if further quantities of the paraffins are added to the crucible, the gold color of the iodine solution disappears in a short time and appears again later. This can be explained on the grounds that unsaturated substances are first formed on decomposition of the paraffins and that they combine with the active iodine. The unsaturated substances resulting from thermal decomposition form peroxides which cause the low ignition point of the paraffins.

With dehydrated lignite tar, the first peroxide formation occurred at about 350°C . With oil from lignite tar, freed from paraffin, peroxide formation occurred at about 350°C and was slower than with pure paraffin. In addition, peroxide formation was established with the following: turpentine oil, and gasoline from petroleum (uncertain).

Various petroleum products were investigated. Work on stearic acid was done at about 300°C . With shale oil, the formation of unsaturated compounds was so appreciable that the iodine previously formed was taken up again. If fresh iodine is added to the solution, it will be immediately absorbed and the solution will again become colorless. With cyclohexanol detection of peroxides was not possible, whereas the decomposition products of methyl cyclohexanol combined with iodine added to

the potassium iodide solution. With benzene and xylene, neither liberation nor absorption of iodine occurred. Naphthalene produced iodine-absorbing decomposition products. Aniline formed a large amount of peroxide and the iodine liberated was not absorbed by the decomposition products, the temperature in this investigation being about 500°C.

These peroxide-forming substances with such properties could be added to oils which ignite with difficulty and thus cause an explosive substance to be formed in the motor which, furthermore, is more effective than the initial igniter usually used. However, peroxide formation appears to decrease with increasing pressure or to be entirely annulled, for under pressure small quantities of peroxide forming substances do not cause further lowering of the ignition point. The phenomena reminds one of the behavior of phosphorus in oxygen, where only under a certain oxygen partial pressure does a luminous reaction occur.

The oxygen reactions before ignition, described above, have hitherto been too little considered. It was only known that the ignition point is frequently lower with substances not readily inflammable, that easily decomposable substances in which the C-C linkage is looser than the C-H linkage ignite the easiest, and that in an homologous series, the ignition point decreases with increasing size of molecule. It was assumed that loosening of the vapor molecules occurred in a direction determined by their chemical constitution and the valences made reactive

through this loosening caused a sudden absorption of oxygen, that is, ignition took place.* Thermal decomposition can even occur to a small extent on ignition in Diesel engines, where frequently only 0.01 second can be assumed for it. It is therefore not possible, as Wartenberg** also emphasizes, for the entire or a greater part of the fuel to decompose before ignition in the Diesel engine. Thermal decomposition and the activity of the compounds thereby formed are alone not sufficient to explain autoignition, in particular with substances which themselves ignite at a much lower temperature. If, on the other hand, it is assumed that the original substances or their thermal decomposition products, within the rapid pressure and temperature rise, take up oxygen to form molecular oxides which, in consequence of their stability, exist only during a short, rapidly passing pressure and temperature interval before they suddenly decompose, then it can be supposed that the ignition of the entire fuel is affected by the shattering power of this decomposition of the very small quantities of such substances. Besides the information obtained in the experiments on iodine liberation, other striking phenomena agree in indicating that autoignition follows the formation of molecular oxides, particularly in the case of substances with a low ignition point. Among such phenomena are the variable effect of pressure on the ignition point; the great sensitivity, already mentioned, of some substances

*Wollers & Ehmke, Krupp. Monatsh., 1921, p. 19.**Zeitschrift des Vereines deutscher Ingenieure, 68, 153 (1924).

which give different values on fluctuation of the barometric pressure; the circumstance that the ignition point of many substances rises with increasing partial pressure of oxygen; and the fact that the ignition point in air at 5 atmospheres is in general not equal to that in oxygen.

Since oxygen compounds which influence the reactions originate before and during the burning, we considered the measurement of the ignition points of pure oxygen-containing substances to be important and we measured them systematically.

As has been already mentioned, those substances which even in the cold form addition products with molecular oxygen, have the lowest ignition points of which we are aware. Thus, for example, the aldehydes have proportionately low ignition points (See Part II, Technical Memorandum No. 484, Table VIII). Further, acetaldehyde has the lowest of all ignition points as yet determined. This holds equally for benzaldehyde. Whereas the remainder of the aromatics have in general very high ignition points, benzaldehyde ignites at a proportionately lower temperature. Autoignition in air occurs at 180°C and in oxygen at 168°C , whereas benzoic acid in air does not ignite even at 650°C , and in oxygen ignition occurs at 590°C . Formaldehyde constitutes an exception as the first number of a series, for it does not behave as the above-mentioned aldehydes, and has in contrast to them a very high ignition point. The ignition points of aldehydes, in air and oxygen, are brought together in the following table:

	<u>Ignition point</u>	
	In air °C	In oxygen °C
Formaldehyde	478	423
Acetaldehyde	185	140..
Propylaldehyde	280	260
Valeraldehyde	417	300
Salicylaldehyde	372	262
Benzaldehyde	180	168

As is evident, salicylaldehyde has a significantly higher ignition point than benzaldehyde. This is understandable since salicylaldehyde is a much more stable compound chemically than is benzaldehyde, and is appreciably more difficult to oxidize. The ketones have on the average very high ignition points. Acetone, for example, does not ignite in air even at 650°C, while in oxygen it ignites at 568°C.

The readily oxidizable ethyl ether, which forms a known peroxide, has a very low ignition point. The difference between the ignition points in air and in oxygen is in this case significantly greater than with the aldehydes. Thus ethyl ether ignites in air at 343°C, which is relatively high, and in oxygen, on the other hand, even at 178°C.

In connection with the ignition points of the alcohols the first member of the series, methyl alcohol, here again shows a different behavior than its homologs.

	<u>Ignition point</u>	
	In air °C	In oxygen °C
Methyl alcohol	-	555
Ethyl alcohol	558	425
Propyl alcohol	505	445
Isopropyl alcohol	590	512
n-Butyl alcohol	450	385
tert-Butyl alcohol	-	500
active Amyl alcohol	409	390

As is apparent, these alcohols have a very high ignition point. The behavior of the isomeric alcohols is interesting. Isopropyl alcohol has an appreciably higher ignition point than the isomeric normal propyl alcohol. The polybasic alcohols have apparently high ignition points. Thus, for example,

	<u>Ignition point</u>	
	In air °C	In oxygen °C
Glycerin	500	414
Mannit	475	400

The ignition points of the unsaturated alcohols are interesting in contrast to the corresponding saturated alcohols.

	<u>Ignition point</u>	
	In air °C	In oxygen °C
Allyl alcohol	367	406
n-Propyl alcohol	505	445
Isopropyl alcohol	590	512

Allyl alcohol ignites in air at a lower temperature than in oxygen. Compared with propyl alcohol from which it differs only through a double bond, the difference in the ignition points in air is very large, whereas those in oxygen are apparently similar.

As with the previous substances, the first member of the homologous series of acids shows a different behavior, as is generally the case in organic chemistry. That is, formic acid has so high an ignition point that neither in air* nor in oxygen up to 680°C can an ignition point be obtained. In the following table, the ignition points of the acids in air and oxygen are brought together.

*Either this statement or the value of 650°C given in the table immediately following for the ignition point in air appears to be in error. - Tr.

	<u>Ignition point</u>	
	In air °C	In oxygen °C
Formic acid	650	above 680
Acetic acid	665	560
Heptylic acid	602	260
Nonylic acid	391	250
Lauric acid	533	275
Palmitic acid	425	245
Stearic acid	430	250
Undecylenic acid (unsaturated)	338	245

Here it is again seen that a double bond (undecylenic acid) gives a remarkably low value, particularly on ignition in air. The acid anhydrides have lower ignition points than the corresponding acids. They show the following behavior.

	<u>Ignition point</u>	
	In air °C	In oxygen °C
Acetic anhydride	585	432
Butyric anhydride	320	370
Valeric anhydride	320	365

In this case also two substances, butyric and valeric anhydrides have ignition points in oxygen higher than in air. The knowledge of the ignition points of acids and their anhydrides is important

since we can assume that they can appear as intermediate products in the combustion.

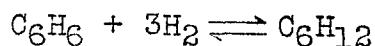
With substances which cannot form oxygen derivatives, the ignition points are usually high and frequently at temperatures where hydrogen is split off. The hydrogen then obviously starts the ignition. This is the case with aromatic hydrocarbons. The ignition point of aromatic hydrocarbons with side chains is lowered and indeed, the longer the chain, the greater the lowering, as is true in general, the properties of aromatic substances with long side chains tending to approach those of aliphatic substances.

3. The Supersaturated State of Organic Compounds

Preliminary Communication by J. Tausz

The saturation characteristics of hydrocarbons are not only a function of the constitution, but also of the temperature and the pressure. In general, hydrocarbons are divided into saturated and unsaturated, as is the case with organic compounds, on the whole. We do not, however, agree with this subdivision, in particular if higher temperatures and pressures are considered, for under those conditions it can happen that a hydrocarbon can give off hydrogen. I choose to designate the hydrocarbon in this case as supersaturated and thereby express the idea that the carbon skeleton is overloaded with hydrogen.

It is important, therefore, to note that an organic compound does not come under one of these states, but that each compound can exist in each of the three states depending upon the temperature and pressure. By increasing the temperature, an unsaturated substance can be changed into a saturated one. With further increase in temperature, this becomes supersaturated. For example, at 180° and ordinary pressure, benzene is an unsaturated substance, which particularly in the presence of catalysts, takes up hydrogen and is quantitatively transformed to cyclohexane. At 300°C, benzene is saturated. Hence the various equilibriums between benzene and cyclohexane can be written



At 180°C, the reaction proceeds mainly from left to right. Between 180°C and 300°C, various equilibrium states exist between benzene and cyclohexane. At 300°C, the reaction proceeds almost quantitatively from right to left. At still higher temperatures benzene is thus supersaturated. Two benzene rings react by splitting off hydrogen and forming diphenyl. The supersaturated condition in this case affects the ignition in so far as it introduces the hydrogen split off.

In an homologous series, the supersaturated state occurs at lower temperatures as the molecular weight increases, so that the paraffins with high molecular weights reach supersaturation at lower temperatures than those of low molecular weight. Since

substances in the supersaturated state are most reactive, the peculiar apparent behavior of paraffin hydrocarbons during the first moment of ignition is intelligible. The paraffin hydrocarbons with high molecular weight have a lower ignition point than those of lower molecular weight. Thus, for example, solid paraffin ignites at about 410°C whereas hexane first ignites at 487°C .

Further, on increasing the pressure, the temperature range of the saturated, unsaturated and supersaturated states is displaced.

It is therefore readily conceivable that the change in the saturation characteristics with change in temperature and pressure is of significance in connection with ignition and in particular with the chemical reactions preceding it. At ordinary temperature and pressure, the saturated compounds change over into the supersaturated or unsaturated state, which occurs at measured temperatures and pressures. If in the supersaturated state the substances react readily with oxygen, molecular oxides or peroxides are formed either by producing hydrogen peroxide from the hydrogen split off in the reactive state or by the taking up of oxygen by the compounds formed.

4. Possibility of the Use of Ignition Measurements in Organic Chemistry

Although the ignition point is a complicated phenomenon, and depends on many factors, it is very characteristic for each substance, so that I (Tausz) consider it to be suitable as a new

instrument in organic chemistry and in particular to be of use for the identification of substances which, for example, have no definite melting or boiling points. Pure substances particularly show very sharp and characteristic ignition points.

Clearly the many possibilities of decomposition and reaction determine the ignition since, for example, impurities can act as initial igniters and thus can be very sharply detected. The slightest impurity lowers or raises the ignition point immediately. I mention the interesting fact that in spite of several measurements of the ignition point of pure benzene, it was still not known, since the various workers had actually investigated no chemically pure benzene, as they attributed no great significance to this point. With ordinary benzene, we also reproduced the previously measured value of 570°C . However, chemically pure benzene had an ignition point of 662°C , a much higher temperature. This is entirely general, if the substance under consideration has a very high ignition point. The basis for this is easily inferred from the initial ignition mentioned above.

Compounds which already contain oxygen or sulphur ignite the most readily. They frequently only need to be mixed in traces with a hydrocarbon as so often happens or with any other less reactive, high-igniting substance in order to act as an initial igniter and thus they indicate their presence.

For various substances, not only is the temperature characteristic but also is the manner of ignition and it includes in-

formation whereby the substances can be very accurately known or differentiated. Between the addition of the igniting material and the occurrence of the explosion a time interval elapses, which we term the time lag. Here naturally the velocity of the reactions taking place before ignition is significant as well as the explosive limits of the air or oxygen mixtures. The flame originating at the ignition point has various forms and sizes. The most intensive illuminations are perceptible when oxygen is used.

Since the difference in the ignition points in air and in oxygen is particularly characteristic, it is recommended that both measurements be employed for purposes of identification. Substances which in air have approximately equal ignition points frequently show very great differences in oxygen and inversely. Often there is no difference between the ignition points of a substance in air and oxygen. For the most part, the oxygen ignition point is lower than that in air, but that is not always the case, as already mentioned, for there are apparently many substances which have a higher ignition point in oxygen than in air. How this is possible, can be explained as follows. In the case of measurements in oxygen the primary substances formed before ignition can take up more oxygen than when in air, and the more strongly oxidized bodies thus formed have a higher ignition point. Substances also occur which have two ignition points, in between which lies a temperature range where only silent combustion occurs.

Research is still in progress on the influence of the presence of water vapor on the ignition point and on the shortening of the time lag by overstepping the lowest temperature at which autoignition still occurs. The time lag especially must be eliminated in investigations on fuels for the purpose of estimating their utility in combustion engines, since ignition in the engine occurs momentarily and therefore designation of the ignition point as the lowest temperature is really not significant, but rather is the lowest temperature at which ignition still occurs with the necessary velocity, that is, momentarily after the addition of the substance.

In order to check the apparatus and to establish comparability with work in other places, substances which were easily obtainable in very pure form were investigated and adopted as calibration substances. Since the sucrose used in calorimetric measurements is also very well qualified for this purpose, although it does not belong to those substances which ignite undecomposed and extensive decomposition and chemical reactions occur before it ignites, it demonstrated that the reproducibility and sharpness of the ignition point was not influenced by the reactions mentioned. It is also evident therefrom that the most favorable composition of the mixture is always present in some one place in the crucible and from there ignition spreads.

Finally a probable connection of the ignition point with the physiological phenomena of combustion should be mentioned

here. Almost all foods have a low ignition point as compared with many substances acting as metabolic poisons, such as benzene, kerosene, acetone and so on, which have a very high ignition point. That chemically pure benzene (ignition point 662°C) is significantly more poisonous than technical benzene (ignition point 570°C), is a known fact which was not clear until now. Turpentine oil acts as an antidote to kerosene and benzene, the ignition points of which are very markedly lowered by small additions of the former.

5. Critical Review of Previous Work on Ignition Points and Combustion Reactions in Diesel Engines

Rieppel* made an interesting "Research on the Use of Tar Oils for the Operation of Diesel Engines," and in order to find the basis for the different behavior of oils, he measured among other things, their specific gravity, heating value, viscosity, flash point and burning point, paraffin content, elementary composition and boiling range. However, none of these measurements gave a definite criterion. The useful oils had a larger hydrogen content, yet Rieppel recognized that this was only an external basis and that the internal one is to be sought in the fact that readily igniting aliphatic hydrocarbons contain more hydrogen than the aromatic ones which ignite with difficulty.

He considered therefore that the hydrogen content, given by the

*Zeitschrift des Vereines deutscher Ingenieure, 1907, p. 618.
Mitt. Forsch. Verein. deut. Ing. 55, (1908).

elementary analysis, was fundamental since out of that a conclusion could be drawn with regard to the presence of known quantities of aliphatic or aromatic hydrocarbons. In general, this still is accepted to-day.

Rieppel also wanted to measure the autoignition temperature (ignition point) under pressure, but did not accomplish it, however. Instead of this, the vapor pressure of oils at different temperatures and the formation of oil gas were investigated. This work led to the conclusion that the formation of oil gas has a decided influence on the utility of an oil for Diesel engines. This is, however, a false inference. Rieppel explained this on the basis that hydrogen was split off, which ignited even at 500°C and so initiated autoignition of the residual molecules.* According to this work, it was believed that the key to the evaluation of the utility of motor oils in Diesel engines was to be found in their different behaviors on heating in a bomb. These conclusions were worked out exhaustively by Neumann** and accepted by Riedler - Löffler.*** Rieppel also sought to find an inexpensive operating substance by mixing good fuel oil with coal tar. His practical results agree with our ignition point results on mixtures under pressure (See Part II, Technical Memorandum No. 484 - table of Experimental Results of Series B (Figs. 8-12) and will be discussed further.

*According to Wartenburg, hydrogen ignites first at 642°C , while according to our work it ignites at 630°C (in oxygen).

**Zeitschrift des Vereines deutscher Ingenieure, 62, p.706 (1918).

***Olmaschinen, Berlin, 1922.

The first person to recognize fully the practical significance of autoignition temperatures and to determine the ignition points of various fuels,* was Holm.** He measured the ignition points with the following apparatus: "In the cylindrical heated space of a Hereaus tube furnace was placed in an upright position along the vertical axis of the porcelain tube an inverted glazed porcelain crucible cover. On the cover was located the bare soldered junction of a Pt, Pt-Rh thermocouple, which indicated the temperature on a suitable galvanometer. A slow stream of air passed through the combustion chamber. The liquid fuel was allowed to fall in drops on the cover, while solid fuels were pulverized, and the cover was heated by 10° intervals until ignition occurred." This apparatus did not yield accurate values and Holm considered it practically impossible to create a technique which would permit accurate reproducibility and to measure for each substance an absolutely definite autoignition temperature.

On comparison of the ignition points of gases and liquid fuels obtained by him, it was remarkable that the tendency towards autoignition frequently did not parallel the inflammability. One should at first think that a combustible gas is subject

*The ignition of gases was studied exhaustively by Dixon, among others. We limit ourselves in this work to the ignition of liquid or solid substances at ordinary temperatures. Our researches on the ignition of gases are still in progress and are reserved for later publication.

**Z. angew. Chem., 26, p.273 (1913). Constan and Schl  pfer had previously concluded a similar research, the results of which were, however, published later (Z. angew. Chem., 26, 352 (1913) and Z. Verein. deut. Ing., 1913, 1491.)

to the influence of the oxygen which supports the combustion on account of the mutual penetration and better contact of the parts, more so than with a liquid or solid fuel. But nevertheless, in general, gases showed a higher ignition point than solid substances of high molecular weight and Holm recognized that another factor must be significant for the origin of autoignition. This factor was regarded as the activity of the free valences on decomposition of the fuel through transformation, cleavage, and rearrangement. Although he could observe the silent combustion occurring before ignition, he attached no significance to it, and disputed before all the importance of using unsaturated compounds because "double bonds in themselves are stable at relatively high temperatures in free oxygen, as the ignition points of liquid fuels with ethylenic bonds and as ethylene itself shows. The splitting off of hydrocarbon groups from saturated chains is in any case greater, therefore a saturated paraffin decomposes and ignites at low temperatures."

It is known, however, through the study of cracking processes and other investigations that even on decomposition of a paraffin unsaturated hydrocarbons in addition to saturated, always result. Thus the paraffin hydrocarbon $C_{12}H_{26}$ decomposes into hexane C_6H_{14} and hexylene C_6H_{12} , and we can establish that the ignition point of a paraffin of approximately this composition corresponds actually to that of hexylene. The activity of ethylene is also significantly smaller than that of its homologs. The ac-

tivity of the free valences on decomposition, emphasized by Holm, is the cause of the origin, already discussed, of oxygen compounds and molecular oxides, for on decomposition of a paraffin, olefinic compounds, along with saturated ones, always form and as already mentioned, these can form molecular oxides the most readily. That the decomposition alone cannot cause the low ignition point, results also from the work of Wollers and Ehmke* which indicates that the decomposition products produced in the absence of oxygen ignite much higher than the original substances of high molecular weight. That fuels, which already contain oxygen, such as turf, cellulose, and lignite, ignite much lower than carbon and anthracite, is further evidence for and not against our views.

That the ignition point is independent of the boiling point, vaporization, flash point, burning point, and so forth, has been emphasized by Holm. The influence of catalysts on gases is very great and not completely eliminated and it decreases with increasing size of the fuel molecules.

Simultaneously with Holm, Constam and Schlapfer** independently examined the utility of various fuel oils and measured among other properties their ignition points. They used a platinum crucible which was placed inside of another larger one, the intervening space being filled with sand. The crucible was covered with an asbestos cover provided with a notch for a Pt,

*Krupp. Monatsh. Jan., 1921.

**Zeit. des Verein. deut. Ing. 57, 1489 (1913).

Pt-Rh thermocouple and a gas inlet tube. It was heated by means of a small Bunsen flame. For a very large number of liquid fuels there were measured in addition to the ignition point, the specific gravity, viscosity, flash point, burning point, heating value, asphalt content, elementary composition, boiling range, composition of fractions and mechanical impurities. At the same time, the oils were tested in the Diesel engine. Constan and Schläpfer did not reach any uniform viewpoint, but are of the opinion that all of the physical and chemical properties must be considered; which would only be possible on the basis of a complete investigation. But according to their researches, none of the factors named was definitely significant, so that there only remained the undertaking of work with the engine itself. Constan and Schläpfer declared that the measurement of the autoignition temperatures was not suitable for an evaluation of utility. They could be used at most for differentiating between different classes of fuel oils. As an example, they quoted that an unsuitable oil ignites at a lower temperature than a suitable one. On consideration of the tables it is seen, however, that the difference in the ignition points with the fuel oils investigated existed only with the measurements in air and that with the measurements in oxygen, they had already disappeared so that it can readily be imagined that the curves of the ignition points intersect with increasing partial pressure of oxygen and that the better oil, igniting at a higher value at ordinary pressure,

will ignite at a lower value in the engine under high pressure. By measuring the ignition point under pressure, values would therefore be obtained which would compare with the behavior in the engine. Later we will return to this in connection with our work on the effect of pressure.

Constam and Schläpfer also measured the ignition point in nickel and porcelain crucibles. Since the values in the nickel and platinum crucibles agreed, while those in the porcelain crucible were much higher, they considered the latter to be incorrect. Since, however, nickel as well as platinum are good catalysts, particularly for the ignition of hydrogen, which is formed from the decomposition of coal tar oil, among others, as Wollers and Ehmke showed, the values obtained in the porcelain crucible are the more correct, particularly with high igniting substances. According to Constam and Schlapfer, the fundamental difference between the two classes into which Rieppel divided fuel oils is that coal tar oils before they ignite must experience an extensive decomposition, whereas the combustion of petroleum and lignite tar oils are initiated by inflammation of their vapors. From much other work, it results, however, that even those substances which must experience an extensive decomposition, like paraffin, for example, ignite lower than their homologs in which decomposition before ignition is less. One must rather seek the explanation on the basis that the decomposition of coal tar oil first takes place at a higher temperature, whereas, for ex-

ample, with paraffins, decomposition occurs already at lower temperatures and thereupon, besides hydrogen, there are formed unsaturated substances which react readily with oxygen.

Moore* measured ignition temperatures with an iron block heated by a gas flame and containing a recess in which a platinum crucible was placed. The thermocouple was situated in a hole in the iron block. By this means the temperature distribution was significantly improved and the catalytic effect of the thermocouple was avoided. On the basis of the values found, Moore computed the resulting theoretical final compression pressure. As already mentioned, no such calculation is permissible. The computed pressure actually does not agree with the lowest pressure obtained in the engine.

Wollers and Ehmke have improved the ignition point apparatus of Moore and have produced an apparatus which is known as the Krupps Ignition Point (for a description, see Part II, Technical Memorandum No. 484, p. 11). They have measured the ignition points in oxygen only and have obtained results consistent, on comparison, with earlier measurements. In opposition to Constam and Schl  pfer, they consider that the ignition point is of great importance in the evaluation of fuel oils. For the theory of the process, they annex the conception of Holm. They assume that mixtures igniting equally high at atmospheric pressure will also ignite equally high at high pressure, which as we can prove, is not entirely correct.

*Journal of the Society of Chemical Industries, 1917, p. 109.

From the standpoint of our investigation, the most important result of the work of Wollers and Ehmke is the refutation of the conception generally held since Rieppel and Neumann, that vaporization and gasification (oil gas formation) is of fundamental significance in connection with ignition in the engine. Wollers and Ehmke produced gaseous products from various fuel oils at various pressures and temperatures with the apparatus of Neumann and measured the ignition temperatures of these gases in Dixon's apparatus. It was thereby established that the ignition points of such gases were relatively high and that with low igniting substances, the original substance ignited much lower than the gaseous products. The following table is taken from Wollers and Ehmke.*

Fuel oil	Ignition temperature of the oil gas in oxygen with the Dixon furnace	Ignition temperature of the fuel oil in a stream of oxygen in I.P. tester of Moore
Paraffin oil	614 - 655°	240°
Light oil from native tar	615 - 651°	326°
Tar oil	645°	445°
Vertical oven tar	635 - 661°	468°

Thus the gaseous products do not show the differences which are noted on use of the fuel oil in the engine. Also vaporization cannot be of influence since the ignition point frequently lies under the boiling point. It must therefore be con-

*Krupp. Monatsh., 2, 14 (1921).

cluded that oil gas formation does not act in the Diesel engine in the manner considered by Rieppel and Neumann. (According to Wartenberg, the temperature in the combustion chamber before ignition is too low and the time much too short for pyrogenic decomposition to occur.)

The basis, therefore, for the conclusion that the ignition points in the open crucible, although they are not significant for conditions under pressure, still afford a criterion for the behavior of fuel oils in the Diesel engine, even though gasification is meaningless, is that the heating in the engine as in the crucible takes place in an atmosphere containing oxygen and before the ignition, primary oxygen compounds are formed, which as our ignition point measurements on pure substances show, have a very low ignition point and thus they influence the sudden pressure and temperature increase and finally the quick combustion of the entire fuel.

The oil gas formed on heating the fuel oil in a bomb included decomposition products which formed in the absence of oxygen and had a high ignition point. Aliphatic fuel oils produce little hydrogen and much ethylene. Aromatic fuel oils produce much hydrogen and almost no olefines. According to our work, the ignition points of aromatic fuel oils are higher than is given in the preceding table and in fact they are approximately as high as the gaseous products, since with aromatic fuel oils the ignition point is actually determined by the hydrogen split off. It

is hardly to be assumed that thermal decomposition does not occur at all and that the combustion, as Wartenberg thinks, only proceeds during the short time immediately in the vapor envelope around the drops and that the drops remain over until combustion is complete. According to this conception, sudden combustion on great velocity of reaction with oxygen is inconceivable for it would not come fully into intimate contact with the fuel molecules. Much more frequently, thermal decomposition occurs and the resulting products, in particular the olefines, react to form oxygen compounds such as molecular oxides. The primary substances thus formed initiate ignition, even if they are formed first in very small quantities, and they undergo sudden decomposition, thereby effecting significant temperature and pressure rises and resulting in a further scattering and more intimate contact of the fuel molecules with oxygen.

With fuels which produce almost no olefines in gasification experiments, but hydrogen and methane in large quantities, it can be assumed that the hydrogen initiates the ignition, although this is exactly in opposition to the conception of Rieppel already mentioned on the less useful fuels. Their ignition points are correspondingly in the neighborhood of the ignition point of hydrogen.

Wartenberg* is of the opinion that immediately on ignition the first quantity of vapor which is developed burns and surrounds the drops as a burning envelope. The oxygen must diffuse through

*Zeitschrift des Vereines deutscher Ingenieure, 68, 153 (1924).

this shell in order that further vapor may burn. The velocity of burning would be limited by the physical process of vaporization and by the diffusion of oxygen. Around each burning drop a shell is formed out of the products of combustion, water and carbon dioxide, produced in the first instant, through which the fresh air must diffuse, if the diffusion path can be made small through relative motion of the air and the drops. Accordingly, fuels which need little oxygen ignite easily while with others, the ignition depends on the hydrogen content.

However, this does not happen. Olefinic hydrocarbons ignite much more readily than saturated ones and indeed, the easier the more double bonds and the less hydrogen they contain. As Wartenberg correctly emphasized, complete vaporization and extensive pyrogenic decomposition is not possible during the short time of 0.01 second. According to our opinion, however, it is inconceivable that ignition proceeding so rapidly can depend on the diffusion of oxygen. One must rather differentiate sharply between ignition and completion of combustion. For the one fineness of subdivision has a great effect, but much less for the other. The work of Haber and Wolff* have shown that combustion is more incomplete, the larger the drops. With fine subdivision, the completeness of combustion can therefore be very much favored. But as the explosive limits do not change thereby, neither does the ignition point, that is, the temperature at which ignition occurs

*Z. angew. Chem., 36, 373 (1923).

or the compression pressure which must be produced (See Part II, Technical Memorandum No. 484, p. 11).

Hawkes* has devised an experimental arrangement for the measurement of the ignition temperature and pressure adapted to conditions in the Diesel engine. He investigated with it only a single oil, namely, shale oil of specific gravity 0.86 at 16°C. After he had determined by work with a Diesel engine that the ignition delay in the engine amounted on the average to 0.04 sec., he conducted work at different temperatures and pressures with the above-mentioned apparatus until the ignition delay of 0.04 sec. was attained. In this manner, the so-called practical ignition point of shale oil, used under the given hypothesis, was measured. The change in the ignition delay with increasing temperature was exhibited by means of a curve. Whereas the lowest temperature at which ignition still occurred was 206°C with a delay of 3.5 sec., ignition at 350°C occurred immediately, that is, within 0.04 sec. This is the "practical ignition point" referred to, as Hawkes terms it.

To be followed by Technical Memorandum No. 484, Part II.

Translation by Oscar C. Bridgeman,
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*Engineering, 110, 786 (1920).

